PAPER • OPEN ACCESS

Surface chemistry changes and microstructure evaluation of low density nanocluster polyethylene under natural weathering: A spectroscopic investigation

To cite this article: M Hamzah et al 2018 J. Phys.: Conf. Ser. 984 012010

View the <u>article online</u> for updates and enhancements.

You may also like

- <u>Chemiluminescence and reactivity of the</u> <u>composites based on blends of</u> <u>polypropylene and polyamide</u> N V Vorontsov, A A Popov and A L Margolin
- Polymer photosensitizing systems containing porphyrins, dinitrosyl iron complexes, and sodium alginate in the generation of singlet oxygen O V Sadykova, N A Aksenova, N N Glagolev et al.
- <u>Laser-induced fabrication of nanoporous</u> <u>monolayer WS₂ membranes</u> Gopinath Danda, Paul Masih Das and Marija Drndi





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 13.58.60.192 on 10/05/2024 at 14:28

Surface chemistry changes and microstructure evaluation of low density nanocluster polyethylene under natural weathering: A spectroscopic investigation

M Hamzah^{1,2}, M Khenfouch³, A Rjeb², S Sayouri², D S Houssaini^{2,4}, M Darhouri² and VV Srinivasu¹

¹ Chair for Superconductivity Technology, Department of Physics, College of Science, Engineering and Technology, Florida campus, University of South Africa, Cnr Christiaan de Wet & Pioneer Avenue Florida 1709, Johannesburg, South Africa

² LPTA, Faculty of Sciences Dhar el Mahraz, University Sidi Mohammed Ben Abdellah,

Laboratory of Theorical and applied Physics LPTA, PO Box 1796 Atlas Fez 30 000, Morocco ³ Africa Graphene Center, Physics department, Eureka building, College of Science,

Engineering and Technology, Florida campus, University of South Africa, Cnr Christiaan de Wet & Pioneer Avenue Florida 1709, Johannesburg, South Africa

⁴ Department of Industrial Engineering, Faculty of Sciences and Technicques, University Sidi Mohammed Ben Abdellah, BP 2202 Fez, Morocco

Corresponding author: hamzah.13.mohammed@gmail.com

Abstract. Polyethylene is the most commonly used plastic in daily life, covering wide areas of application e.g. this polymer is used as a greenhouses covering material. This article investigates the effect of photo-oxidation on commercial unstabilised Low Density Polyethylene (uLDPE), as result of outdoor weathering factors. In this study, the samples were exposed for four months to the natural weather. The physico-chemical effects of natural ageing were studied by attenuated total reflection Fourier transform infrared (ATR-FTIR) and X-ray photoelectron (XPS) spectroscopy to elucidate the chemical composition, the nature of chemical bonds established and further to interrogate the changes that occur on the surface of the uLDPE samples. The main chemical change of uLDPE results in the formation of different kinds of carbonyl and vinyl groups identifiable in the ATR-FTIR and XPS spectra. The degree of crystallinity for these samples was calculated in terms of time exposure. An increase in the degree of crystallinity due to chemicrystallization was observed, which we indicative of the occurrences of chain scission. During outdoor exposure it was found that the photo-oxidation results in the formation of chain scission occurrences via Norrish type II reactions.

1. Introduction

For many decades, polymers have been increasingly used across various fields in divers sectors. Today, the areas of application are still in continuous expansion due to the wide range of uses that polymers serve in commercial; and industrial markets. The choice of using a polymer instead is often motivated by cost reduction in conjunction with a reduction in weight, without sacrificing performance. Amongst synthetic polymers, polyethylene and polypropylene are extensively used in the polymer industry and alone represent more than 50% of the total volume of the thermoplastics manufactured in the world. In view of the importance of polyethylene, the study of its performance characteristics have been carried out for many years.

Polyethylene is the polymer with the largest production and commercial uptake within the sector. Low density polyethylene (LDPE) is particularly well known for its use in many outdoor applications, especially for greenhouses, as covering material. Unfortunately, the polymers (polyolefins) are subject

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution **(ii)** of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd

to natural (outdoor) weathering, which lead to material degradation. Weathering is particularly severe for organic materials, because it combines the photophysical and photochemical effects of ultraviolet (UV) radiation, with oxidative effects of atmospheric oxygen and the hydrolytic effects of water [1]. Weathering is commonly defined as the undesirable change produced by outdoor exposure [1]. The study of the aging of polyethylene through weathering is of great importance for the development of more resistant materials, in comparison to what was previously available. For this reason, many studies have been conducted over the years, for instance, to investigate the natural aging of polyethylene [2-11], and to study the artificial aging [12-16].

The photodegradation of polymers is mainly caused by the introduction of chromophores, such as catalyst residues, hydroperoxide groups, carbonyl groups, and double bonds, during polymer manufacture [17]. Studies on the luminescence polymers have expanded the field of knowledge about the absorption of molecules and, therefore, on photooxidation mechanisms. Charles by et al. [18] were the first to report the phosphorescent emission of polymers containing carbonyl impurities. Allen et al. [19] were interested by the phosphorescence of species formed during the thermal oxidation and photo-oxidation process for commercial polyolefins. They observed the presence of species having an excitation wavelength in UV-B range. These authors attribute this phosphorescence to ketones and aldehydes which would, according to them, the main initiators of photo-oxidation [19]. Photochemical initiation (photolysis ketones) is responsible for the formation of various oxidation products, the photolysis of ketones proceed according Norrish I and Norrish II reactions.

Polyethylene is a semi-crystalline polymer, the most stable crystal structure of polyethylene and most commonly encountered corresponds to an orthorhombic crystal lattice [20]. On a morphological point of view, polyethylene can be considered as alternating crystalline and amorphous layers (two-phase system). Oxidation damage confined to the amorphous phase causes the break of the tie molecules that link the various crystalline lamellae, and lead to a sudden loss of microstructural properties at break [21]. The weathering of polyethylene affects the crystallinity. The shorter chains produced during chain scission are more mobile and are able to crystallize more readily, which increases crystallization and associated embrittlement [17, 22].

The current work presents the analysis of natural ageing behavior of uLDPE samples. Aging characterization was performed by attenuated total reflection Fourier transform infrared (ATR-FTIR) and X-ray photoelectron (XPS) spectroscopy. In this study we discussed the contribution of photolysis ketones reactions according Norrish I and II, we used ATR-FTIR spectroscopy to monitor changes in crystallinity during natural weathering. changes Complementarily to infrared spectroscopy, the aging behavior was investigated by using XPS spectroscopy, which is useful to study the determination of atomic composition of the surface of aged unstabilised polyethylene, therefore the level of oxidation of the surface may be assessed. Furthermore, and by means of the deconvolution of the carbon and oxygen, the XPS spectra indicate the variety of the bonds.

2. Experimental

2.1. Materials

The commercial uLDPE agro films was kindly supplied by the Algerian company ENIP (Entreprise Nationale des Industries Petrochimiques) without additives, having as trademark: PEBD B21 ENIP. The density and the melt flow index given by the supplier are respectively d=0,923 g/cm³ and 0,019 g/min. The samples were about 20x20 mm. The unaged sample was analyzed by ATR-FTIR and XPS spectroscopy and served as reference.

2.2. Natural (outdoor) weathering

The samples uLDPE have been weathered under natural sunlight (days and nights) for four months during the period from July to October. Natural aging of these samples was carried out at the roof of a building in Fes city, Morocco. The average temperature varied between 18 and 34°C and the daily average was 26°C, the relative humidity average was 41%. This period was chosen because the climate is hot and dry. The samples were then placed on wooden board (100x100 cm), the board was then placed on roof top facing southwards at 45 angle with the roof or plane of the earth in accordance with NF T-51165. The samples directly exposed to the weather were taken out monthly and characterized regularly by ATR-FTIR and XPS spectroscopy.

2.3. Material characterization

2.3.1. Attenuated total reflection Fourier transform infrared spectroscopy

ATR-FTIR spectra were recorded on a Magna-IR 560 using ZnSe crystal. The spectra were recorded in the 400-4000 cm⁻¹ range, with a resolution of 4 cm⁻¹ and scan number of 400. All spectra were taken in logarithmic absorbance mode. Experiments are performed applying the ATR equipment with the FTIR spectrometer. The sample surface exposed to photo-oxidative conditions has been in contact with ZnSe crystal.

The spectral bands of the investigated functional groups of the polymer were normalized with respect to a reference band and internal standard. Obviously, the reference band was present in unstabilised polyethylene samples and its intensity and wavelength did not change upon the aging time. The band characteristic of the wagging deformation of methylene groups (1368 cm⁻¹) was accepted as the reference band [13,23,24]. The relative intensity of a specific absorption band was calculated as the ratio of the surface area of this band to that of the reference band.

Infrared ATR spectroscopy provides a qualitative and quantitative analysis of the chemical functions present in the surface. The qualitative analysis was based on separation of the peaks by means of a Lorentzian fitting of the infrared spectra in the region 1600-1800cm⁻¹ and 1000-1250 cm⁻¹ using OriginPro8 software. The quantitative analysis was performed using the peak surface areas. The quantification of the different photo-oxidation products was carried out by means of calculation of carbonyl and vinyl index according to the following equations:

$$I_{\text{carbonyl}} = \frac{A_{C=O}}{A_{1368}} (1)$$
$$I_{\text{vinyl}} = \frac{A_{C=C}}{A_{1368}} (2)$$

Where $A_{C=0}$, A_{909} and A_{1368} are respectively the areas peaks of carbonyl group (1670-1800 cm⁻¹), the area peaks of vinyl group 909 cm⁻¹. These indexes were normalized using the peak at 1368 cm⁻¹. The study of the crystallinity changes for orthorhombic uLDPE after weathering has been determined

by the infrared spectroscopy. The rate of crystallinie content X_{cr} was calculated via the empirical equation of Zerbi et al. [25]:

$$X_{\rm cr} = 100 - \frac{((1 - I_a/I_b)/1.2333)}{(1 + I_a/I_b)} \ 100 \qquad (3)$$

Where X_{cr} percentage of crystalline content, I_a represents the area peaks corresponding to polyethylene crystalline content (729 cm⁻¹ or 1472 cm⁻¹), and I_b represents the area peaks corresponding to the amorphous content (719cm⁻¹ or 1462 cm⁻¹). The constant 1.2333 corresponds to the relation of the intensities of these bands for a completely crystalline polyethylene.

2.3.2. X-ray photoelectron spectroscopy(XPS)

The XPS set-up used was a Kratos Axis Ultra system with an electrostatic-magnetic hybrid lens. The sample is fixed on a stainless steel sample holder, using stainless steel screws also. A surface of about 400x800 μ m was analyzed by a monochromatic Al K α source at incidence angle of 30°. The base pressure analysis chamber is 8x10⁻¹⁰Torr. When recording data, the pressure rises to a value of 5x10⁻⁹ Torr. During the analysis of peaks, we used Shirley background, and for all spectra, the Gaussian/Lorentzian ratio was 40. Calibration of XPS survey spectra were based on the C1s peak, while the calibration of C1s spectra was based on the peak Csp3 and calibration of O1s spectra of the peak C-OH.

For the unaged sample, the XPS analysis was performed without cleaning. For the aged samples, there has been cleaning with distilled water and drying with compressed air before the measurements.

3. Results and discussion

3.1. Attenuated total reflection Fourier transform infrared spectroscopy

3.1.1. Structural modifications and chemical changes

The usual bands of pristine uLDPE are located in the regions: 3000-2800, 1550-1400 and 750-650 cm⁻¹ [26], and are illustrated in figure 1, we are in the presence of three strong absorption bands.

1) The two peaks of the doublet 2846 and 2914 cm⁻¹, with a very strong intensity, correspond to the vibration mode of the chain CH_2 groups [7, 14], respectively assigned to the methylene symmetric and asymmetric C-H stretching vibration [26-28].

2) The two peaks of the doublet 1462 and 1472 cm⁻¹, with a strong intensity, are ascribed respectively to the bending deformation of methylene CH_2 groups in amorphous and crystalline domains respectively [29,30].



Figure 1. ATR-FTIR spectrum of the non-aged uLDPE.

3) The two peaks of the doublet 719 and 729 cm⁻¹, with a strong intensity, are assigned to CH_2 rocking deformation [26, 30-32] in amorphous and crystalline domains respectively [27, 30].

In addition to these three usual bands above, there are also three peaks that have low intensity in the region 1390-1320 cm⁻¹ (figure 1). The peak in 1377 cm⁻¹ ascribed to CH₃ symmetric deformation [26, 31], the peak 1368 cm⁻¹ and 1351 cm⁻¹ inset are assigned both to the wagging deformation CH₂ group [13, 23,24,26].

After defining characteristic bands of the virgin uLDPE sample that have not undergone the natural aging (figure 1), we have followed the progress of degradation, with the exposing time, of uLDPE samples under the influence of weather (natural climatic conditions). Due to aging, new peaks appear alongside usual bands characterizing the C-H bond,-CH₂-, and CH₃ groups (figure 2); we define three regions containing different bands that varied clearly upon the natural aging (figure 3A, 3B). We will discuss simultaneously the peaks that reveal these regions.



Figure 2. ATR-FTIR spectra of uLDPE for different times of exposure to natural aging. (a) non-aged, (b) aged one month, (c) aged two months, (d) aged three months, (e) aged four months.

IOP Conf. Series: Journal of Physics: Conf. Series 984 (2018) 012010

In the region 850-1000 cm⁻¹ (figure 3A), we observe after two months of exposure, the emergence of a small peak of low intensity to 877 cm⁻¹ and one month later (sample d), next to the latter peak appear a second peak at 909 cm⁻¹ with similar intensity. In the final stage of aging (sample e), we find that the small peak at 909 cm⁻¹ persists and the other around 877 cm⁻¹ disappears (figure 3A). The peaks at 877 and 909 cm⁻¹ correspond to vinylidene (-CH=CR₁R₂) and vinyl (-CH=CH₂) respectively [3, 23,33]. The consumption of the vinylidene group is known to be due to their reaction with alkyl radicals (RH) which leads to the formation of crosslinks [21]. These results are in perfect agreement with those established by Chabira et al. [21].



Figure 3. ATR-FTIR spectra of uLDPE samples for different times of exposure to natural aging. (A) In the region 850-1250- cm⁻¹, and (B) In the region 1600-1800 cm⁻¹, (a) non-aged, (b) aged one month, (c) aged two months, (d) aged three months, (e) aged four months.

In the region 1000-1250 cm⁻¹ (figure 3A), the first signs of the aging effect appear in this region, which is known as an amorphous band [5]. Amorphous regions are prone to oxidative chain scission [35]. After two months of exposure appears a peak around 1031 cm⁻¹ related to the formation of the C-O bond due to oxidation processes. This latter peak after three and four months shift to 1040 cm⁻¹ and about 1045 cm⁻¹ respectively (figure 3A).



Figure 4. Fitting of the ATR-FTIR spectrum of uLDPE aged during four months of exposure to natural weathering in the region 1000-1250 cm⁻¹.

The diffusion of oxygen through the amorphous regions is much easier than in the crystalline regions [37]. Oxidation damage confined to the amorphous phase causes the break of the tie molecules that link the various crystalline lamellae [21]. In the third month, near the peak at 1040 cm⁻¹ rises two peaks 1110 and 1177 cm⁻¹ with small intensity (figure 3A). In the last stage of aging, we have performed a Lorentzian fitting to separate and identify all the peaks (figure 4). We have identified four peaks 1045, 1065, 1110 and 1177 cm⁻¹ are ascribed respectively to the stretching vibration of CH₂-O group [7,14], the stretching vibration of the C-C bond in the amorphous phase of the polyethylene [36], the stretching vibration of the C-O bond due to the ether group C-O-C [27], and the latter peak is assigned to the stretching vibration of the C-O bond characteristic of the ester group [27], which is also defined by the C=O bond that we will see in what follows.

In the region 1600-1800 cm⁻¹ (figure 3B), until the second month we have a complete absence of peaks. In the third month of aging (samples d), the 1712 and 1730 cm⁻¹ are correlated with the presence of carbonyl absorption band [37]. One month after (samples e) the vinyl group at 1660 cm⁻¹ appears in the vicinity of the carbonyl groups and is assigned to C=C stretching vibration [27]. The formation of carbonyl groups and vinyl groups can be interpreted as a direct indication of main chain scission [37,38].



Figure 5. Fitting of the ATR-FTIR spectrum of uLDPE aged during three months of exposure to natural weathering in the region 1600-1800 cm⁻¹

In order to highlight the nature of chemical bonds between atoms (functional group), and also to identify and monitor the carbonyl band which is an entanglement of compounds, a Lorentzian fitting was performed for the last two months of natural aging. The figure 5 shows that after three months of exposure there is no trace of vinyl group, no peaks in the 1600-1670 cm⁻¹. In the carbonyl region 1670-1800 cm⁻¹ we distinguish two carbonyl compounds, 1712 cm⁻¹ is assigned to ketone group, and 1730 cm⁻¹ is belonged to aliphatic ester group [27,34,39] both carbonyl groups are ascribed to the stretching vibration of C=O bond. According to Barbara Stuart [27], the aliphatic ester group has two polar bonds C = O and C-O respectively in the bands 1750-1730 and 1300-1100 cm⁻¹. Indeed, we have defined previously the stretching vibration of the C-O bond at 1177 cm⁻¹characteristics of the aliphatic ester (figure 3A and 4). This result is more or less similar to that evoked by Yang et al. [40] who had attributed the ester group to the peaks 1741 and 1178 cm⁻¹. Furthermore, Tijani [37], in his study of linear low density polyethylene under different natural and accelerated weathering conditions, assigned the peak at 1735 cm⁻¹ to esters, and noted that the only apparent difference observed compared to spectra obtained in accelerated aging, is related to the esters groups: the shoulder at 1735 cm⁻¹ have a lower intensity in natural aging. In the last stage of natural aging, by means of fitting (figure 6) in addition to ketone and ester groups, a small peaks of γ -lactone (1780 cm⁻¹) and vinyl groups (1660 cm⁻¹) appears. The fitting also exhibit that after four months of exposure, the area of IOP Conf. Series: Journal of Physics: Conf. Series 984 (2018) 012010

ketone group is smaller than that of ester group (figure 6). This result can be due to the formation of the vinyl group which derived from the photolysis of the ketone according to Norrish II reaction.



Figure 6. Fitting of the ATR-FTIR spectrum of uLDPE aged during four months of exposure to natural weathering in the region 1600-1800 cm⁻¹

3.1.2. Quantification of the photo-oxidative products

The study of the evolution of vinyl and carbonyl degradation products gives a good indication of the progress of the polymers aging. In particular, some studies have shown that the amount of carbonyl can be directly correlated with the degradation of the polyethylene [41-43]. After having identified the carbonyl groups via fitting, we focus on the quantification of carbonyl and vinyl degradation products. The measurement of vinyl and carbonyl groups formation involves the calculation of the indexes previously defined I_{Vinyl} and I_{carbonyl}. Table 1 gives the evolution of these components, includes three carbonyl species and shows their evolution over time. We find that there is nothing to report for the first and second months of exposure; the absence of carbonyl massif is also clearly seen in the figure 3B. In the third month the amount of ketone is quite important, the ester group is also present, but with a smaller amount compare to this of ketone. At this stage the ketone index is almost double that of the ester. After three months of exposure γ -lactone appears and its index was calculated to be 0.62, and the vinyl index increases. Moreover, we note that the index for the ester increases linearly until a maximum value in the fourth month, however, the index of ketone decreases.

Natural aging time		vinyl Index			
	Ketone Index	Ester Index	γ-lactone Index	Vinyl index	
One month	-	-	-	-	
Two months	-	-	-	-	
Three months	2,54	1,36	-	0,12	
Four months	0,57	4,14	0,62	4,52	

Table 1. Carbonyl and vinyl index depending on the exposure time of uLDPE to natural aging.

3.1.3. Microstructural evaluation: crystallinity changes

The increase in carbonyl and vinyl groups formation in polyethylene after weathering is known to be proportional to the number of chain scissions that occur in the polyethylene [17,22]. Effect of chain scissions induced crystallinity modification. Therefore, another way for characterizing degradation and

following the microstructural changes after weathering is to monitor the crystallinity variation of polyethylene samples, which is a good indication of the chain scissions mechanism. Moreover, the mechanical behavior of semi-crystalline polymers, such as low density polyethylene, is directly dependent on the microstructure. Different parameters can influence the mechanical behavior of these materials such as the rate of crystallinity or the size and distribution of crystallites [44].

Table 2 illustrates the variation of the crystalline content of LDPE samples versus the natural aging time via the empirical equation of Zerbi et al. [25] defined before on equation (3). We can notice a considerable difference in terms of selected bands (table 2). The intensity ratio 729 cm⁻¹/719 cm⁻¹ leads to a crystalline content ranging from 59.60% to 66.81%, and the bands 1472 cm⁻¹/1462 cm⁻¹ leads to crystallinity values between 53.31% and 55.08%. We find that the values of crystallinity, for the band 1472 cm⁻¹, are versatile. Kaci et al. [45] have studied the crystallinity changes of low density polyethylene films exposed to natural weathering using FTIR and DSC and WAXS analyses. They concluded that the measurement of crystallinity through the bands 1474 and 1464 cm⁻¹ attributed to scissoring modes leads to unreliable results. Thus, we will adopt the crystallinity values calculated from the methylene rocking bands at 729 cm⁻¹ and 719 cm⁻¹.

Table 2. Crystalline and amorphous contents evaluated by means of Zerbi et al. Equation using ATR-
FTIR spectroscopy.

Exposure Time (months)	Amorphous content (%)	Crystalline content (%)	I _a Value	I _b Value				
Bande spectrale $I_a = 729 \text{ cm}^{-1}$ et $I_b = 719 \text{ cm}^{-1}$								
0	40.40	59.60	1.0315	0.3454				
3	35.64	64.36	1.323	0.515				
4	33.19	66.81	1.4827	0.6212				
	Bande spectrale $I_a = I_a$	$1472 \text{ cm}^{-1} \text{ et } I_b = 1462 \text{ cm}^{-1}$						
0	46.69	53.31	0.9793	0.2635				
3	46.63	53.37	1.4953	0.4033				
4	44.92	44.08	1.7439	0.5				

The behavior of crystallinity shown in table 2 indicates ascension in the value of the crystalline content from 59.60% for pristine sample, to 64.36%, after three months of exposure. The crystalline content continues to increase to reach 66.81% after four months of exposure, which means an increase of 7.21% due to natural aging of uLDPE. Mendes et al. [46] reported by using thermal analysis DSC, in the case of non-stabilised hight density polyethylene HDPE submitted to a natural aging in Rio de Janeiro, that after 74 days of exposure, they marked 6% increase in crystallinity. Kaci et al. [45] studied the crystallinity of unstabilised low-density polyethylene (LDPE) films under natural weathering conditions in Bejaia Mediterranean town of Algeria, via FTIR spectroscopy, the value of the crystallinity content have increased by 7% after 170 days of exposure. The crystallinity measurements depend on the geographical site which they are submitted, and we can say that for some polyolefins, crystallinity increases with natural weathering exposure.

An increase in crystallinity can also be used as an index of the degradation of polyethylene via chain scissions occurring mainly in the amorphous phase. These latter reduce the density of entanglements in the amorphous phase, which allows shorter molecules to crystallize because of their higher mobility [17,33]. Therefore, the secondary crystallization, takes place in the amorphous phase of the polyethylene. The amorphous phase of the material is characterized by a free portion containing entanglements and a part linked to crystalline lamellae.

3.1.4. Mechanisms of photo-oxidation reactions

Photo-oxidation aging develops under the joint action of ultraviolet light and oxygen, making it a leading cause of the polymers aging. It belongs to the class of chemical aging associated with oxidation phenomena; the action of light produces radicals which subsequently react with oxygen. The absorption of UV solar radiation and the ability of oxygen to diffuse into the material have a crucial role.

The solar radiations reaching at the surface of the earth called UV-B (280-315 nm) are responsible for the majority of polymer degradation [47]. Thereby, Allen et al. [48] suggest that the polyolefins should not be affected by solar radiation. Likewise Gijsman et al. [49] confirm this, and claim that the polyolefins which belongs polyethylene only absorb in the deep UV (λ <200 nm). On the other hand, relying on the absorption of thin films of polymers (0.05 mm thickness) in the UV (220-390 nm), Searle [50] specifies that the aliphatic polymers such as polyethylene and polyvinyl chloride are not able to absorb UV solar radiation reaching the earth, so saturated in the area 280-400 nm. The main absorption band of these polymers would be located, according to the authors, below 220 nm. Guadagno et al. [41] concede the photochemical aging to the absorption of solar radiation by the impurities present in the polymer.

Studies conducted on the polyolefins by luminescence have expanded the field of knowledge about the absorption of molecules and, therefore, on photo-oxidation mechanisms. Charles by et al. [51] were the first to report the phosphorescent emission of polyolefins containing carbonyl impurities. Allen et al. [19] have studied the phosphorescence of species formed during the thermal oxidation and photooxidation process for commercial polyolefins. They observed the presence of species having an excitation wavelength higher than 290 nm. These authors attribute this phosphorescence to ketones and aldehydes which would, according them, the main initiators of photo-oxidation [19]. Therefore, according to these authors, and to our results, we can conclude that the absorption of sunlight, for our samples, may be derived from chromophore groups such as the catalytic residues and carbonyl impurities (ketones) formed during the polymerization phase. Ketones absorption bands would be between 330-220 nm and below 340 nm, and then contribute to the initiation of photo-oxidation. Thus, photolysis of ketones seems to be explained preferentially by Norrish I and II reactions.

We discuss, in what follows, the contribution of ketones photolysis reactions according Norrish I and II. The Mechanism of the photolysis of ketone according Norrish I is a free radical process, leading both to chain scissions and crosslinking, while the photolysis by Norrish II is not a radical process and leads only to chain scissions, accompanied by the production of vinyl groups. The formation of unsaturated vinyl at 909 and 1660 cm⁻¹ (figure 3 and 6) indicates that we are in the presence of Norrish II reaction. In other words, stopping the formation of vinyl attest another way by photolysis of ketones according Norrish I. Thereby, the transition from Norrish II to Norrish I can not occur, since we notice that after three months of exposure, vinyl concentrations always continue to evolve (figure 7 and table 1). On the other hand, the passage of the photolysis of ketones from Norrish II to Norrish I first requires a deceleration of reaction rate of vinyl formation followed by a cessation of the formation of unsaturated vinyl; condition not satisfied in our spectra.



Figure 7. Photolysis of ketones according Norrish II mechanism.

In order to rule on the predominance between Norrish I and II, Carlsson and Wiles [52] studied the photolysis of models ketones: ketone A in mid-chains and ketone Bat the end of chains. They concluded that ketone A is photolyzed primarily by a Norrish type I scission to give carbon monoxide and two macroradicals. Whereas ketone B is photolyzed by a Norrish type II scission to give Ketone

IOP Conf. Series: Journal of Physics: Conf. Series 984 (2018) 012010

and an unsaturated polymer chain end. This proves again that the mechanism of photo-oxidation of our samples is made according to Norrish II process, and that it is ketones at the end of chains.

After discussing the predominance of reactions Norrish I and II one over the other, we are looking now to focus our study on the consequences of these reactions. The effects of photo-oxidation on macromolecular scale could be summed up in the competition of two phenomena: the formation of chain scission and crosslinking. The kinetic of these two phenomena is governed by Norrish I and II mechanisms. The crosslinking reactions derived from Norrish I process are in reality bridges of dioxygen formed by reaction between peroxyl radical and vinyl. Thus these possible reactions also could explain the decrease in vinyl concentration. Indeed, Pagès et al. [53] observed by IR analysis, after 60 days of HDPE exposure to natural aging, a decrease of absorbance vinyl groups they attribute to crosslinking. This case is not convenient to our results (table 1), the vinyl index increase with exposure time, and consequently the mechanism of photo-oxidation follows Norrish II process. Chain scissions reactions could arise from β scission of alkoxyl radical [54-56], and from photolysis of ketones according Norrish type I and II. A production of chain scission through β scission of alkoxyl radical is excluded, since we have no traces of aldehydes and acids in our spectra (figure 6). In the second case, the formation of chains scission according Norrish I is marginalized, as long as vinyl groups are still present in the final stages of aging. So we are left with the possibility of the origin of the chain scission mainly occurs through photolysis of ketones according Norrish II mechanism.

3.2. X-ray photoelectron spectroscopy

The XPS surveys of uLDPE samples in figure 8 are used to identify the kinds of atoms present in the surface. Figure 8 shows the presence of an intense peak with the maximum at 285 eV assigned to the carbon atoms C1s, that is the main constituent on the surface of the unaged samples and for the others polyethylene samples aged under natural weathering during four months. Oxygen (O1s at 532 eV) is the major contaminant compared to other surface elements, and the intensity of the corresponding peak increases during the aging. Minor contaminants are also found, mainly small peaks of silicon (Si2p at 102 eV and Si2s at 153 eV), and aluminum (Al2p at 75 eV), we can attributed these contaminants to the clays which can be carried by the wind and settle on the surface of our samples during natural aging.



Figure 8. XPS survey spectra of uLDPE samples. (a) non-aged; (b) aged during one month; (c) two months; (d) three months and (e) four months.

Especially, illite is dominant in Fes (northern Morocco) clays, but is associated with kaolinite [57]. A peak of carbon Auger is also present at 986 eV, obviously, hydrogen was also present in the samples but it is undetectable with the XPS technique. The characteristic feature of the recorded survey scans is that the intensity of the O1s peak increases with exposure time and that of carbon decreases (figure 8 and figure 9).

Table 3 gives the percentages of atomic concentrations of the chemical species present on polymer surfaces. Carbon peak C1s remains the main constituent on the surface for all the samples (figure 8, table 3), but their atomic concentration decreases during natural aging. However, the trend of the

evolution of oxygen concentration is the opposite of that of carbon, in the first stage for the unaged polyethylene it was very low, after that increases during the aging process to the detriment of C1s, which points out the increasing oxidation level of the sample surfaces. For the aluminum and silicon their atomic percentage increase notably with the duration of the aging, we notice that the amount of silicon is twice as that of aluminum (table 3), this may be related to the stoichiometry of clay as illite. The percentage of the others elements present at the surface are present with very small amounts less than 1% such as nitrogen, sodium and magnesium. The exposition to natural weathering affects the state of sample surfaces, after four months the higher percentage of oxygen indicates that the surface of the material had oxidized.

 Table 3. Atomic concentrations (%) of the different elements constituting the surface of the uLDPE for different exposure times under natural weathering.

Atomic concentration (%)							
uLDPE samples	C1s	O1s	Al2p	N1s	Si2p	Chemical elements (<1%)	
Non aged	99.1	0.66	0.06	0.09	0.08	-	
One month	84.69	10.38	0.15	1.11	0.36	Na, Fe, Ca, S, Mg, Cl	
Two months	82.54	12.45	1.09	0.28	2.13	Na, Fe, Ca, S, Mg	
Three months	75.72	16.6	1.75	0.59	3.34	Na, Fe, Ca, S, Mg, Cl	
Four months	64.79	23.95	3.05	0.67	5.26	Na, Fe, Ca, S, Mg, Cl	



Figure 9. Evolution of percentages of the atomic concentrations of the C1s and O1s peaks according exposure time.

After the presentation of the quantitative analysis results, it is interesting to conduct a qualitative analysis, which provides more details. The study of the surface will be focused on the evolution of the main components, the peaks centered on the C1s (energy range 280-291 eV) and O1s (energy range 530-538 eV). The qualitative analysis is carried out by the decomposition of the peaks associated to C1s and O1s, thus the C1s and O1s XPS spectra will allow us to identify carbon and oxygen atoms in regard to their chemical environment, and to confirm the mechanism responsible of photo-oxidation aforesaid.



Figure 10. [A]: XPS spectra, centered on the C1s level of the uLDPE samples, aged during three months. [B]: XPS spectra, centered on the C1s level of the uLDPE samples, aged during four months.

Figure 10A shows the results of such decomposition of the peaks relative to C1s corresponding to the uLDPE sample aged during three months. The spectrum has been treated to correct the charge effect due to the insulating nature of the sample. This correction has been done by setting the $-CH_n$ bonding energy at 285 eV. The C1s peak was deconvoluted into five subpeaks, zoom was performant in the range 291-287 eV to see clearly the subpeaks in this range (figure 10B). We distinguished five subpeaks located at 284.6, 285, 286.6, 288 and 289 eV (figure 10B). The subpeak at 285.4 eV is assigned to C-C or C-H bond, so related to the carbon atoms forming the polymer chain (Csp3) and the peak at 284.7 is a Csp2. The others subpeaks represent the bonding of carbon to oxygen, respectively C-O (286.6 eV) [58], O-C-O or C=O (288 eV) [59, 60] and O=C-O (289 eV) [60]. After four months of natural aging (figure 10B), we noticed that the subpeaks attributed to the carbon-oxygen simple bonds increased implying that surface oxidation had occurred. The peak associated to combined double and single bonding, O=C-O is more intense than the one related to double bond C=O.



Figure 11. [A]: XPS spectra, centered on the O1s level of the uLDPE samples, aged during three months. [B]: XPS spectra, centered on the O1s level of the uLDPE samples, aged during four months.

The results of the qualitative analysis for oxygen atoms presented by the XPS spectrum of O1s (figure 11A) for the polyethylene weathered during three months can be decomposed in three subpeaks 532, 532.8 and 534 eV. The three subpeaks are related only to oxygen bonds with carbon, and are belonging respectively to C=O (532 eV) [60], C-OH, O-C-O or COOR (532.8 eV) [59,61] and O=C-O (534 eV) [62]. The others bonds like oxygen-silicon, and oxygen-aluminum are neglected. Figure 11B shows the O1s spectrum after four months of weathering, the observed differences are just quantitative; the oxygen simply bonded to the carbon atom remains the main contribution. The oxygen atom of esters groups their contribution increase to the detriment of ketones groups. The previous mechanism of photo-oxidation has been proposed for the purpose to interpret the existence of the different bonds formed by oxygen.

4. Conclusion

ATR-FTIR and XPS spectroscopy have been used to study the surface chemistry changes of the unstabilised polyethylene under natural weathering, in a quantitative and qualitative manner. By means of the X-ray photoelectron spectroscopy, the quantification of the products formed in surface of the polyethylene samples was determined with good accuracy, and then it was possible to follow the evolution of the atomic concentrations of carbon and oxygen atoms of aged polyethylene. Moreover, various chemical elements present on the polymer surface with low concentrations were unveiled. Through the deconvolution of the C1s and O1s peaks, the qualitative analysis provides information about the chemical environment of the carbon and oxygen atoms, and then we come to know the nature of bonds established. Comparing these results to that of ATR-FTIR, we conclude the mechanism of photo-oxidation of our samples is made according to Norrish II.

ATR-FTIR spectroscopy has been used to understand structural modifications, and to monitor carbonyl and vinyl groups formations, and to determine crystallinity changes during weathering. Structural changes after weathering were investigated by following carbonyl group, and vinyl group formation, which increase as exposure increase. The calculated vinyl group index can also be used to indicate polymer chain scission. Indeed, chain scission occurs during exposure, as evidence by growth of carbonyl and vinyl groups. Furthermore, an increase in crystallinity indicates the polyethylene chain scission during the photo-oxidation. Increase in crystallinity can occur if chain scission occurs; consequently, the polymer experienced a secondary crystallization, which takes place in the amorphous phase. The origin of the chain scission mainly occurs through photolysis of ketones according Norrish II mechanism.

Acknowledgments

Special thanks to the Innovation city of USMBA (Morocco), Nanosciences African Network, University of South Africa Department of Physics, iThemba Labs (South Africa), African Laser Center and Africa Graphene Center.

References

[1] Feldman D 2002 J. Poly. Environ. **10** 163

- [2] Rabek JF 1996 Phys. charact. applications
- [3] Scoponi M, Cimmino S and Kaci M 2000 Polymer. 41 7969
- [4] Hassini N, Guenachi K, Hamou A, Saiter J M, Marais S and Beucher E 2002 *Poly. Degrad. Stab.* **75** 247

[5] Szép A, Anna P, Csontos I, Marosi Gy, Matko Sz and Bertalan Gy 2004 *Poly. Degrad. Stab.* **85** 1023

[6] Sqalli Houssaini D, Rjeb A, Rjeb M, Sayouri S, Roy D, Massey S and Sadoun T 2007 *J. Catal. Mat. Env.* **VI** 213

[7] Boulos Y, Dehbi A, Hamou A and Marc Saiter J 2008 Mater Des. 29 2017

[8] Massey S, Adnot A, Rjeb A and Roy D 2008 *Plast. Rubber Compos.* 37:7

[9] Darhouri M, Sqalli Houssaini D, Rjeb A, Rjeb M, Sayouri S, Roy D, Massey S, Sadoun T and Laoutid F 2009 *Phys. Chem. News.* **47** 40

[10] Hamzah M, Rjeb A, Sqalli Houssaini D, Sayouri S and Massey S 2011 Phys. Chem. News. 58

[11] Hamzah M, Rjeb A, Sqalli Houssaini D, Sayouri S and Darhouri M 2013 *Phys. Chem. News.* 70

[12] Carrasco F, pages P, Pascual S and Colom X 2001 *Eur. Poly. J.* **37** 1457

[13] Kupper L, Gulmine JV, Janissek PR and Heise HM 2004 Vib. Spectrosc. 34 63

[14] Dehbi A, Bouaza A, Hamou A, Boulos Y and Marc Saiter J 2010 Mater. Des. 31 864

[15] Grabmayer K, Wallner GM, Beißmann S, Braun U, Steffen R, Nitsche D, Roder B, Buchberger W and Lang RW 2014 *Poly. Degrad. Stab.***109** *40*

[16] Schwarzinger C, Hintersteiner I, Schwarzinger B, Buchberger W and Moser B 2015 J. Anal. Appl. Pyrolys.. **113** 315

[17] Jabarin SA and Lofgren EA 1994 J. Appl. Poly. Sci. 53 411

[18] Charlesby A and Partridge RH 1965 Proceedings of the Royal Society of London. Series A: Math. Phys. Sci.283 312

[19] Allen NS, McKellar JF and Phillips GO 1974 Poly. Lett. Edition 12 253

[20] Peacock AJ 2000 Handbook of polyethylene Structures, Properties, and Applications. By Marcel Dekker

[21] Chabira SF, Sebaa M, Huchon R and De Jeso B 2006 Poly. Degrad. Stab. 91 1887

[22] Wypych G 1995 Handbook of material weathering.2nd ed. Ontario, Canada: Chem Tec Publishing

- [23] Zenkiewicz M, Rauchfleisz M and Czuprynska J 2003 Rad. Phys. Chem. 68 799
- [24] Tertinnikov ON, Fujita SI, Ogata S and Ikada Y 1999 J. Polym. Sci. Part B: Polym. Phys. 37 1503
- [25] Zerbi G, Gallino G, Del Fanti N and Baini L 1989 Polymer. 30 2324
- [26] Gulmine JV, Janissek PR, Heise HM and Akcelrud L 2002 Poly. Test. 21 557
- [27] Stuart B 2004 Chapter 4 Organic Molecules. Wiley 71
- [28] Shi LS, Wang LY and Wang YN 2006 Eur. Poly J. 42 1625
- [29] Wu H and Fan J 2008 *Poly. Test.* **27** 122
- [30] Fu Y and Lim LT 2012 Poly. Test. 31 56
- [31] Oldak D, Kaczmarek H, Buffeteau T and Sourisseau C 2005 J. Mater. Sci. 40 4189

[32] Feuilloley P, César G, Benguigui L, Grohens Y, Pillin I, Bewa H, Lefaux S and Jamal M 2005 *J. Poly. Env.* **13** 349

- [33] Stark N M and Matuana L M 2004 Poly. Degrad. Stab. 86 1
- [34] Gulmine JV, Janissek PR, Heise HM and Akcelrud L 2003 Poly. Degrad. Stab. 79 385
- [35] Craig IH, White JR, Shyichuk AV and Syrotynska I 2005 Poly. Eng. Sci. 45 579
- [36] Vasile C and Pascu M 2005 *Practical guide to polyethylene*. Rapra Technology
- [37] Tidjani A 2000 Poly. Degrad. Stab. 68 465
- [38] David C, Trojan M, Daro A and Demarteau W 1992 Poly. Degrad. Stab. 37 233
- [39] Khabbaz F, Albertsson AC and Karlsson S 1998 Poly. Degrad. Stab. 61 329
- [40] Yang R, Li Y and Yu J 2005 Poly. Degrad. Stab. 88 168
- [41] Guadagno L, Naddeo C, Vittoria V, Camino G and Cagnani G 2001 Poly. Degrad. Stab. 72 175
- [42] Allen N S, Edge M, Holdsworth D, Rahman A, Catalina F, Fontan E, Escalona A M and Sibon F F 2000 *Poly. Degrad. Stab.* **67** 57
- [43] Valadez-Gonzalez A, Cervantes-Uc JM and Veleva L 1999 Poly. Degrad. Stab. 63 253
- [44] Douminge L, Mallarino S, Cohendoz S, Xavier F and Bernard J 2010 Curr. Appl. Phys. 10 1211
- [45] Kaci M, Sadoun T and Cimmino S 2001 Int J Polym Anal. Charact. 6 455
- [46] Mendes LC, Rufino ES, De Paula FOC and Torres Jr AC 2003 Poly. Degrad. Stab. 79 371
- [47] Grossman DM 1998 Surf. Coat. Aus. 25 6
- [48] Allen NS and McKellar JF 1975 Chem. Soc. Rev. 4 533
- [49] Gijsman P and Dozeman A 1996 Polym. Degrad. Stab. 53 45
- [50] Searle N D 2000 Handbook of Polymer Degradation chapter 16. Dekker, 605-643
- [51] Charlesby A and Partridge R H 1965 Series A: Math. Phys. Sci. 283 312
- [52] Carlsson D J and Wiles D M 1969 Macromolecules. 2 587
- [53] Pagès P, Carrasco F, Surina J and Colom X 1996 J. Appl. Polym. Sci. 60 153
- [54] Iring M, Tüdos F, Fodor Z and Kelen T 1980 Polym. Degrad. Stab. 2 143
- [55] Costa L, Luda MP and Trossarelli L 1997 Polym. Degrad. Stab. 58 41

[56] Khelidj N, Colin X, Audouin L, Verdu J, Monchy-Leroy C and Prunier V 2006 *Polym. Degrad. Stab.* **91** 1598

[57] El Ouahabi M, Daoudi L and Fagel N 2014 Clay. Minerals. 49 35

[58] Rats D, Vandenbulcke L, Herbin R, Benoit R, Erre R, Serin V and Sevely J 1995 *Thin Solid Films* **270** 177

[59] Brown N M D, Hewitt JA and Meenan B J 1992 Surf. Inter. Anal. 18 87

[60] Rjeb M, Labzour A, Rjeb A, Sayouri S, Chafik El Idrissi M, Massey S, Adnote A and Roy D 2004 J. *Phys.* Condens. Matter. **5** 168

[61] Rjeb A, Letarte S, Tajounte L, Chafik El Idrissi M, Adnot A, Roy D, Claire Y and Kaloustian J 2000 J. Electron. Spectrosc. Relat. Phenom. **107** 221

[62] Poleunis C, Weng LT, Sclavons M, Bertrand P, Franquinet P, Legras R and Carlier V 1995 J. Adhes. Sci. Technol. **9** 859